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LAMINATED MILD STEEL STRIP

Background of the Invention

Field of the invention

This invention relates to laminated mild steel strip for use especially, but not exclusively, in the packaging industry and to methods of manufacturing such strip. More especially, the invention relates to a method of chemically treating mild steel strip prior to lamination with a thermoplastic material.

Description of Related Art

Organic-coated metal substrates, for example thermoplastic resin-coated tinplate or blackplate, are used, *inter alia*, in the production of packaging materials, for example, food and beverage cans. As a result, organic coatings so used, are required to conform with strict performance criteria. To maintain the integrity of a can as well as to ensure that its contents are maintained in a suitable condition over a storage period which may span months or even longer, the coating must exhibit good stain resistance, corrosion resistance and resistance to delamination.

GB-A-2329608A discloses a process for producing thermoplastic resin-coated aluminium alloy plate in which the plate is treated sequentially with alkali and acid solutions to put the plate surfaces in such a condition that the increase rate of the specific surface area is 3 to 30%. The treated plate is then subjected to an anodic oxidation treatment prior to lamination with thermoplastic resin.

Organic coatings have traditionally comprised solvent or water-based

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lacquers. Recently however, the use of laminated polymer films and coatings, such as thermoplastic resins, has been recognised as a viable alternative.

In practice, organic coatings are not applied directly onto mild steel (otherwise known as blackplate), because for packaging applications the metal surface is too reactive and underfilm corrosion can spread rapidly. Instead, the can-making industry uses *metallic*-coated mild steels, such as tinplate or electrolytically chromium-coated steel (ECCS) as substrates for organic coatings.

Currently, a surface-treated mild steel strip may comprise a chrome/ CrO_x or tin layer electrochemically deposited so that the final substrate has either a metallic chromium layer of typically from 50 to 150 mg/m^2 and a chromium oxide/hydroxide layer of typically from 10 to 30 mg/m^2 , or a layer of metallic tin of typically between 5 and 10 g/m^2 . In many applications it is preferred that tinplate is additionally subjected to chromate solution treatment, the amount of oxidisable chromium being between 1 and 10 mg/m^2 .

Unfortunately, electro-plating pre-treatment is a costly and time consuming process. Not only are materials expensive, but the electro-plating process itself consumes large quantities of energy. In addition, this conventional pre-treatment adds an additional production step in the process line, which adds costs in terms of line-time, manpower and through yield.

It has been shown that for some applications, the degree of protection afforded by the ECCS or tin pre-treatment exceeds the performance requirements of the can. For this reason and the disadvantages associated with electroplating discussed above, there is an increasing desire to develop an alternative metal strip pre-treatment which avoids these problems but maintains the performance requirements of certain classes of food, beverage or aerosol cans. Preferably, any such pre-treatment should be capable of application under

the present day metal strip coating and lamination line conditions.

In the past, there has been a general understanding in the industry that alternatives to electro-deposited tin and/or chrome would afford significantly less substrate protection. However, if a suitable alternative pre-treatment could be found, an electroplating process step would be unnecessary with consequent increases in yield, savings in energy and reductions in the overall production costs of laminated metal strip.

Handwritten: p1 Summary of the Invention
~~It is an object of the present invention to provide a suitable alternative to~~
 conventional electroplating of metal strip prior to coating with an organic resin, which provides adequate corrosion protection of the organically coated metal strip and provides and maintains good adhesion to such organic resin coatings.

According to the present invention in one aspect, there is provided a process for manufacturing laminated mild steel strip, the process comprising the steps of,

- (a) cleaning the strip;
- (b) chemically pre-treating the cleaned strip to form on one or each of its surfaces a non-metallic chemical coating of an oxyanion to resist corrosion of the underlying mild steel substrate and to promote adhesion to a subsequently applied layer; and,
- (c) applying to the chemically-treated strip a coating of thermoplastic resin ~~to form a protective layer on at least one surface thereof.~~

The term "non-metallic coatings" as used herein refers to coatings which despite optionally including *metal ions*, differ from what is conventionally described as a metallic layer in that there is no *native* metal. Unlike a metal layer wherein metal atoms, through metallic bonding, *solely* form a crystalline structure, in the non-metallic coatings of the present invention, both metallic and non-metallic ions are distributed within an amorphous network.

The strip may be cold-rolled mild steel strip. Mild steel strip is conventionally referred to as blackplate.

Typically, the strip has a gauge of between 0.08 and 0.50mm. A preferred gauge is 0.18mm.

Preferably, the strip is cleaned to remove all traces of contamination which may be present as a result of previous cold rolling and annealing processes. Typically, the strip is cleaned electrolytically using a caustic-based solution, although the nature of the cleaner does not influence the subsequent chemical treatment. After cleaning, the strip may be rinsed with water to remove all traces of the cleaning solution.

The chemical coating may be applied to the strip using a conventional application method such as immersion, spraying, roller coating, or a combination thereof.

Typically, the chemical coating is applied by immersing the cleaned strip in chemical contained in one or more treatment vessels. In one embodiment, the strip is chemically treated for less than 60 seconds; in other embodiments, the chemical treatment times are less than 30 seconds or less than 15 seconds. Preferably, the strip is chemically treated for less than 10 seconds; typically, 5 seconds.

Typically, the strip is chemically treated at a temperature of less than 100°C, most preferably at less than 30°C.

In one aspect of the invention, the strip is chemically treated to form a chemical coating which prevents subsequent underfilm corrosion of the strip and promotes adhesion between the strip and thermoplastic resin. The chemical coating may be referred to as a *coupling agent* since it forms a strong

and durable *chemical bridge* at the interface between the metal substrate and the final organic resin coating. The chemical bridge has a dual role; it interacts with receptive inorganic surfaces to form tenacious chemical bonds at the interface with the metal substrate *and* at the interface with the organic resin coating.

P¹ ~~The oxyanion coating may comprise a phosphate, a chromate, an oxalate or an arsenate. Additionally, the coating may comprise yttrium, elements in the lanthanum series of the periodic table, silanes or azoles.~~

When metal substrates are exposed to the atmosphere, the surface of the metal develops a naturally occurring surface oxide layer. Typically, the oxide layer on blackplate at ambient temperature will have an average thickness of between 2 and 20 nm. Thus, in one embodiment, the chemical coating may be applied to the metal oxide layer on the surface of the metal substrate.

P³ ~~The chemical treatment may comprise, for example, zinc orthophosphates, manganese phosphates or iron phosphates, thereby producing crystalline phosphate coatings on the strip.~~

In a preferred embodiment of the invention the strip is chemically coated with a composition comprising less than 5% atomic chromium.

P⁴ *P⁷* After chemical treatment, the strip may be rinsed and/or dried, for example with hot air, prior to treatment with organic resin.

One or more layers of thermoplastic resin may be applied to one or both sides of the chemically-treated strip. The layer or layers of thermoplastic resin may be melted and rapidly quenched to attain the required degree of crystalline structure.

Typically, a film of thermoplastic resin may be co-extruded with the chemically-treated strip to form laminated strip. The film of thermoplastic resin may be bonded to chemically-treated strip under conditions of elevated temperature and pressure.

The chemically-treated strip may be coated with a thermoplastic resin together with a bonding layer. The bonding layer may comprise a polyester, or an acid or acid-anhydride polyolefin resin containing carboxyl or anhydride groups. Typically, the bonding layer is between 1 and 10 μ m thick.

Alternatively, the chemically-treated strip may be extrusion coated with at least one thermoplastic resin.

Preferred thermoplastic resins comprise polypropylene (PP), polyethyleneterephthalate (PET) or a combination thereof.

Typically, the thickness of the layer, or layers, of thermoplastic resin are between 3 and 50 μ m.

The chemical treatment has two functions; firstly it provides corrosion protection and inhibits underfilm corrosion, and secondly, it promotes good adhesion between the organic resin coating and the strip. These properties combined with the barrier properties of the organic coating provide a laminated metal strip product which can be formed into components for a range of applications whilst maintaining adequate performance criteria with regard to corrosion resistance and inter layer adhesion during the lifetime of the products.

Therefore, in another aspect, the invention provides a laminated strip produced by a process which comprises the steps of chemically treating the strip to form on at least one of its surfaces a non-metallic coating, and applying to that coated surface a coating of a thermoplastic resin to form a layer thereon.



  The invention will now be described by way of example only with reference to the accompanying diagrammatic drawings and tables in which:-

Figure 1 is a histogram showing the performance rating of food-filled cans made from PET-laminated and chemically treated blackplate;

Figure 2 is a histogram showing the performance rating of food-filled cans made from PP-laminated and chemically treated blackplate; and,

Table 1 tabulates the conditions, concentrations and dipping times of exemplary chemical treatments.

A process line for producing laminated blackplate comprises a plurality of guide rollers for transporting a strip of blackplate continuously from a coiled roll to an exit coil via a multiplicity of vertical tanks. These tanks include a cleaning tank, rinsing tanks and a chemical treatment tank. The line speed is typically 10 to 100 metres per minute with a treatment dwell time of between 1 to 10 seconds. After hot-air drying, the chemically treated strip is laminated with organic polymeric resin e.g. a thermoplastic resin such as PET at elevated temperature and pressure. The laminated strip is then rapidly quenched to produce an essentially amorphous organic outer coating.

By way of example, the performances of two commercially available chemical treatments (referred to below as chemicals A and B) were evaluated as potential alternatives to the conventional electroplating step in the production of an organically coated mild steel strip.

Chemical A comprised a commercially available chemical treatment comprising chromium, silicon and organic active species. Chemical B comprised a commercially available chemical treatment comprising a two component

organic polymer i.e. an acrylic polymer and $(\text{NH}_3)\text{Cr}_2\text{O}_6$.

In the evaluation, blackplate of 0.08 to 0.50mm thickness was subjected to an electrolytic cleaning process using a commercial cleaning solution at a temperature not exceeding 100°C , by passing a current of 20A for 5 seconds. This treatment is considered to return current densities to approximately 10 Adm^{-2} . The nature of the cleaner employed on the blackplate does not influence any subsequent chemical treatment. It is important that the strip is clean and free of contamination from prior processing. Before dipping in the chemical treatment vessels, the samples were washed in two ambient water rinse tanks. The concentrations of the cleaner and chemical treatments were those recommended by the respective suppliers. A batch of samples exposed only to electrolytic cleaning were also prepared as a control sample group, identified in Figures 1 and 2 as B-plate.

As well as "cleaned only" samples, an ECCS control sample group was also laminated. Samples of both $15 \mu\text{m}$ PET and/or $40 \mu\text{m}$ PP were laminated at elevated temperature and pressure. The hot samples were plunged into cold water just as the current was switched off. Instant quenching of this nature has the effect of retaining the amorphous nature of the thermoplastic coating at ambient temperature. Table 1 illustrates the concentrations, dip times and treatment section temperatures for evaluated chemicals A and B.

Samples of each variable were subjected to a wedge bend test. Both treatments A and B performed equally well; no delamination or cracking of the polymer was observed. A standard Erichsen and cross scored Erichsen were also performed. The samples were evaluated for signs of blisters and/or delamination. Again, both A and B performed well with little to distinguish between them.

About 350, 73mm diameter classic can ends were produced on a

conventional MB20 can end press. Approximately 20 samples of each treatment with both PET and PP were produced. A standard lining compound was applied to each end. Half the ends were lightly scored prior to filling with foodstuff to create a standard defect and potentially allow a greater degree of differentiation of the chemical treatments on opening.

8oz cans (73 x 63mm) were filled with either rabbit cat food or cut green beans in salt brine under standard filling conditions. The cans were stored on their sides at an elevated temperature (37°C). Cans with scored ends were stored with the score running vertically so that it entered the head space area. Four cans of each variable were opened after 2, 5, and 15 weeks. Opened cans were evaluated for sulphide staining, delamination and corrosion (on and off the score line).

The can end performance was judged on three main criteria (sulphide staining, delamination and corrosion (on and off the score line)) using a points system. Three points were awarded if the defect was obviously present and two points if the defect was only minor. No points were allocated if the defect was absent. All points were totalled for each category of defect over the three openings, for both polymer film types and for each chemical pre-treatment. The results are illustrated in Figure 1 and Figure 2.

It should be noted that the performance rating system used here gives equal weighting to each of the attributable defects. Arguably, sulphide staining could be regarded as a less serious defect than delamination as it is only aesthetic and does not directly reflect can performance. Nevertheless, the approach highlights the chemical treatments which perform relatively adequately for use in can-making applications.

In summary, the trials show that chemical pre-treatment in accordance with the invention provides an effective alternative to metallic electroplated

coatings prior to coating of strip with organic resins.

It may be envisaged that in another embodiment of the invention, blackplate can undergo chemical pre-treatment "off-line" with transfer to the lamination line post treatment. However, this is less cost effective due to the necessity for a separate coating facility and any associated transportation or storage costs.

It will be appreciated that the foregoing is merely exemplary of treatments in accordance with the invention and that modifications can readily be made thereto without departing from the true scope of the invention.

TABLE 1

Chemical Treatment	Working concentration	Dip time (seconds)	Temperature of dip °C
A	3%	1	25
B	as supplied	3	< 30